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RESEARCH ARTICLE

EFFECTS OF HISTORIC FLOODONWATER QUALITYOF FRESH WATER RESERVOIR KEENJHAR LAKEOFSINDH, PAKISTAN

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ABSTRACT

Keenjhar Lake(Kalri Lake) located in Thatta district of Sindh, Pakistan. A total number of 27 water samples were taken before and after the historic flood(27-08-2010) from different locations of the study area in year2010. The sampleswereanalyzedto estimatefor the pH, electrical conductivity (EC), calcium (Ca), magnesium (Mg), total dissolved solids (TDS), total suspended solids (TSS), sodium (Na), chlorides (Cl), sulfate (SO_4), phosphate (PO_4), carbonate (CO_3), bicarbonate (HCO_3) and potassium (K)including heavy metals such asiron (Fe), cadmium (Cd), lead (Pb), arsenic (As), chromium (Cr), copper (Cu) and zinc (Zn) for evaluation of the different samples lakewater.This study also determines quality indicators for monitoring of Keenjhar lake water quality factors identified by using statistics on thirteenPhysico-chemical parameters andseven heavy metals.It is a well-known fact that the heavy metal ions are potentially toxic to human health and could be quite detrimental for human life. The study have revealed the pollution status for the area thatheavy metals, As, Cd, Cr andPbare present in slight excess to WHO limits especially after flood spell. While all thirteen physico-chemical parameters resultswere within WHO/EU limits. Hence the water quality of KeenjharLake is not directly potable without proper treatment.

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INTRODUCTION

The world most devastating natural hazards are Floods, which cause substantial damage to economies and social developments as compare to other occurrences. The major historic floods were recorded in the years 1928, 1929, 1955, 1973, 1976, 1980, 1988, 1992 and 2010. Lakes are at receiving side of floods and plays an important role in absorbing the negative effects as well (Mateeul Haq *et al*, 2012). Keenjhar Lake is located in Thatta district, Sindh province, Pakistan. It is 122 km from north east of Karachi and 18 km from the town of Thatta (24°57′N 68°03′E). It is the second largest perennial fresh water lake in Pakistan. Historically, Keenjhar Lake is formed by the union of two lakes, namely Sonehri and Keenjhar. It is an important source of drinking water for more than 200 million people of Karachi city and one million people of surrounding of Thatta District. Karachi gets about 78% drinking water from Keenjhar Lake through 2 canals which were specially built for this purpose. 24 km long, 6 km wide, and has a depth of 26feets, spread over 13,468 hectares. Its total area is 134.7 km^2, Length 24 km, Surface elevation 15 m and Width: 6 km, Water volume: $0.53\times10^{\wedge6}$ acre·ft (650 hm^3) (Wikipedia).Main source of water storage in Keenjhar Lake is Kalri Baghar(KB) Feeder, KB Canal is feeding source of fresh water to the lake and originating from the Indus River. Storage capacity of lake is 7.2 million acre feet(Yahya *et al*, 2016).Water is essential component of all forms of life and it is mainly obtained from two sources, i.e. surface water which includes rivers, canals, fresh water lakes, streams etc. (Mc Murry *et al*, 2004). Lakes are large bodies (i.e., greater than 20 acres) of inland water. Most of the drinking water, as well as water used for irrigation, industry and hydropower come from freshwater lakes and reservoirs in Pakistan including Keenjhar Lake(Islam *et al*, 2019). The lake, however, has steadily declined in both productivity and its freshwater resources chiefly on account of chemical pollution, over fishing and eutrophication (Yahya *et al*, 2016).The annual per capita availability of water was 5,800 cubic meter in 1951 to about 1100 cubic meter in 2006 and projected to 1066 cubic meter in 2010 (Habib, 2008).If the status quo continues, then by 2020, the water availability in Pakistan would further plummeted to 877 cubic meters per

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annum, which will further go down to an alarmingly level of 575 cubic feet in 2050(Mustafa, 2012).Pakistan extracts 74.3 percent of its fresh water annually thereby exerting tremendous pressure upon renewable waterre sources (UNDP Pakistan, 2016).The sources of the heavy metals in Lake can be a release from chemical weathering of minerals, soil leaching processes in addition to anthropogenic activities. These anthropogenic sources include industrial and domestic effluent, landfill leachate and mining activities (Biwas *et al*, 2017).The over burden of the human population, unplanned urbanization, unsustainable and unrestricted abstraction policies and inappropriate dumping of solid as well as liquid wastes, lack of strict enforcement of law and loose governance has resulted in the deterioration of ambient water quality and quantity in Pakistan (WWF, 2007). One third of the world's population is dependent on ambient water for drinking purposes (Nickson *et al*, 2005).It is important to examine the quality of ambient water prior to its particular use (Arumugam, Elangovan, 2009). Investigation of the Odra river flood sediments have shown high metal concentration (Helios-Rybicka *et al*, 1999). Quality of water determines population health (Jianmin *et al*, 2016). According to Karachi Water & Sewerage Board, each day, about 450 million gallon per day (MGD) of water from Keenjhar is supplied to the city (KWSB website). In Pakistan, most of the drinking water about 66% is supplied through metal pipes and hand pumps of which quality is not maintained with the passage of time rusts and various pathogenscause 30% of various health diseases and 40% of deaths just due to poor water quality (Global Water Partnership, 2000).

Pakistan has been blessed by nature with enough surface and ambient water resources. Industrialization, urbanization, and rapid population growth have placed huge stress on water resources (Soomro *et al*, 2011).Due to technological developments, drinking water may contain various impurities, which are of physical, biological and chemical nature. The most dangerous impurity is of biological nature, which causes human health problems or cause death (Park, 2007).Water pollution is a physical process that occurs in various water resources such as lakes, ground water, and rivers due to anthropogenic activities (Agarwal, 2002).The WHO estimated that more than 85 million people do not have access to safe drinking water in Pakistan. It is revealed that in Karachi more than 10,000 people die every year because of renal infection caused by contaminated water.A worldwide survey report on water borne diseases revealed that every third person had become a patient of hepatitis B or C similarly, Sindh province is the most affected by these chronic diseases (PCRWR, 2010).In most of the developing countries, the water sources are non-potable without treatment (Joyce *et al*, 1996). About 50% of all reported cases of illness and 40% of deaths in Pakistan are due to drinking of poor water quality (Chhatwal, 1990, Sanaullah *et al*, 2014).

MATRIALS AND METHODS

***Experimental Instrumentations*:** Various physicochemical parameters were analysed by conventional titration methods and using pH meter (Orion 720A), HACH 44600 conductivity/TDS meter, UV-spectrometer Thermo (Evolution 300),Flame photometer (Sherwood Scientific^{TM} M410 C), UV spectrophotometer (Perkin Elmer Lambda 2) and atomic absorption spectrophotometer-AAS (Hitachi Model 5000 Z)were used.

Reagents and glasswares: Ultrapure water obtained from Milli purifier system (Millipore crop Bedford, MA, USA) was used throughout the study. All chemicals were of analytical reagent grade and obtained from E. Merck (Darmstadt, Germany). Concentrated nitric acid and hydrogen peroxide were used for the digestion of samples. Working standard solutions were prepared immediately from stock standards. All solutions were stored at 04 °C until needed for analysis. Plastic and glasswares were cleaned by soaking in 2M of HNO_3 solution for overnight. (Panhwar *et al*, 2019)

Sampling: The water samples were collected in high density polyethylene (HDPE) bottles1.5 liters capacity,which had been thoroughly washed and filled with distilled water, and then taken to the sampling site. The samples were collected from three sampling stations for a period of ten months from February to December, 2010. A total of 27 samples (9 samples from inlet, 9 from mid area of Lake and 9 from outlet) were collected in triplicate manner from the three sampling sites namely Chull site (Inlet), near grave of Noori (Mid) and Chilya (Outlet). All samples were collected in three monitoring visits and nine samples in each visit were taken and all samples were labeled properly, placed in an icebox to preserve the inherent characteristics of the water. Standard procedures have been used for the collection, transportation, storage and chemical analysis of the samples.

***Measurement of Physico-chemical parameters*:** Various physicochemical parameters such as pH by the pH meter, TSS &TDS by gravimetric analysis, SO_4 by precipitation gravimetric method, EC by the conductivity meter, K & Na by the photometer, PO_4 the UV-spectrometer and rest of chemical parameters like Cl, CO_3,HCO_3, Ca andMg were analyzed by conventional titration methods as per Standard Methods for the Examination of water and wastewater(APHA).

***Measurement of Heavy Metals*:** The Heavy metals Fe, Cu and Zn were evaluated by Flam technique of AAS. Whereas, Cd, Pb and Cr were determined by Graphite Furnace AAS. The Hydride formation AAS technique was also utilized for arsenic (As) analysis as per Standard Methods for the Examination of water and wastewater (APHA).

Statistical Analysis: All experimental data were examined in triplicate and calculations (mean+std) were done through MS Excel Software.

RESULTS AND DISCUSSION

The results of the current study shows that the condition of the water is not highly affected by pollution before flood. The pH value of water indicates whether the water is acidic or alkaline. Water with a pH value ranged from 6.5 to 8.5 is generally considered satisfactory for drinking purpose. pH results of all samples were between 7.37 to 8.2 and found within range as per table 1.EC of water is an index to represent the total concentration of soluble salts in water (Harilal *et al*, 2008). It represents the ability of water to conduct an electric current. Electrical Conductivity was found within the limits except sample No. 7 of final round that indicate more ions in upstream after flood.

Table1. Physico-Chemicals Results of Water Samples

Parameters		18-02-10		16-07-10				09-12-10		WHO Guideline Values
	1	2	3	4	5	6	7	8	9	
pH(1-14)	7.37	8.19	7.94	8.2	7.96	8.04	7.95	8.17	8.15	6.5-8.5
EC(µS/cm)	550	508	516	485	467	463	1328	845	844	--
TDS	383	378	385	314	320	327	665	457	459	1000
TSS	8.2	7.6	7.6	6.5	4	0.5	9.6	6.4	8.7	--
Chloride	44	38	44	43.4	46.2	47.5	157	97	96	250
Phosphate	45.3	44.6	47.5	26.7	21.4	23.5	29.5	23.7	22.5	--
Sulfate	66	67	61	53	54	55	151	71	72	--
HCO3	74	75	79	51	52	54	43	83	84	--
CO3	1.2	1.1	1.3	0.4	0.5	0.5	0.5	7	5	--
Na	34.1	33.5	34.7	28.3	30	32	97	47	48	200
K	5.4	5.2	4.8	4.4	4.7	4.8	10.3	7	7.5	--
Ca	52	53	52	46.3	49.3	49.1	93	91	92	--
Mg	44	45	44	43.4	44	43.5	54	32	33	--

Table 2. Results of Heavy Metals of Water Samples

Parameters	18-02-17				16-07-17			09-12-17		WHO Guideline Values
	1	2	3	4	5	6	7	8	9	
	Inlet	Mid	Outlet	Inlet	Mid	Outlet	Inlet	Mid	Outlet	
Fe	0.127	0.101	0.104	0.153	0.162	0.161	0.376	0.174	0.173	0.2
Cd	0.0036	0.0043	0.0083	0.003	0.002	0.001	0.0235	0.0123	0.0122	0.005
Pb	0.0038	0.0029	0.0029	0.007	0.005	0.005	0.0596	0.023.9	0.0204	0.01
As	0.001	0.002	0.002	0.003	0.004	0.003	0.029	0.017	0.016	0.01
Cr	0.004	0.009	0.009	0.011	0.009	0.008	0.149	0.105	0.104	0.05
Cu	0.053	0.036	0.075	0.016	0.014	0.012	0.586	0.439	0.438	2.0
Zn	0.042	0.038	0.039	0.023	0.013	0.012	0.725	0.583	0.581	--

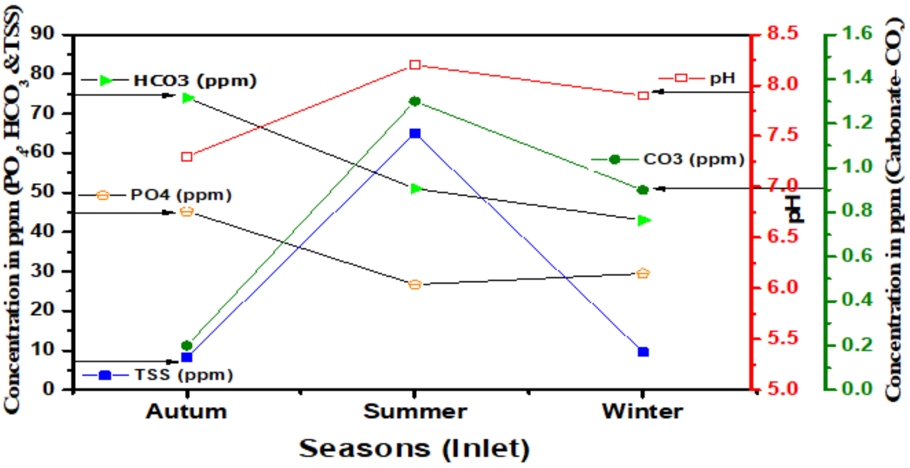

Fig.1a Seasonal effects onphysico-chemical parameters at inlet

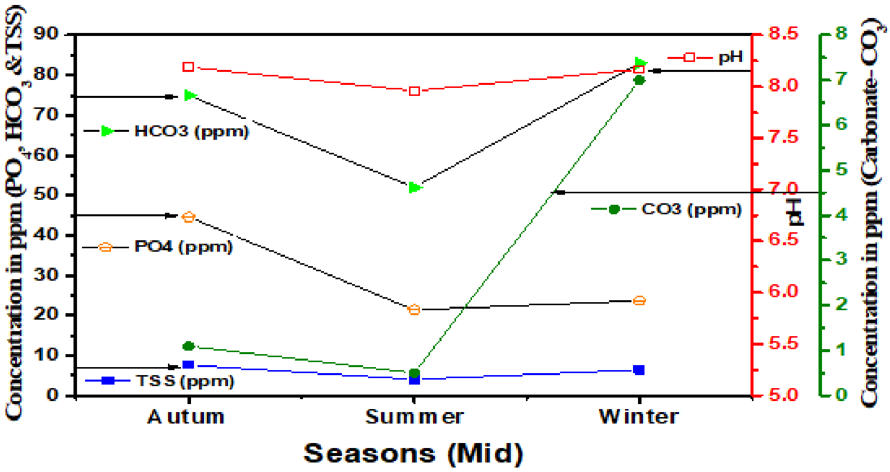

Fig.1b Seasonal effects on Physico-Chemicals parameters at mid

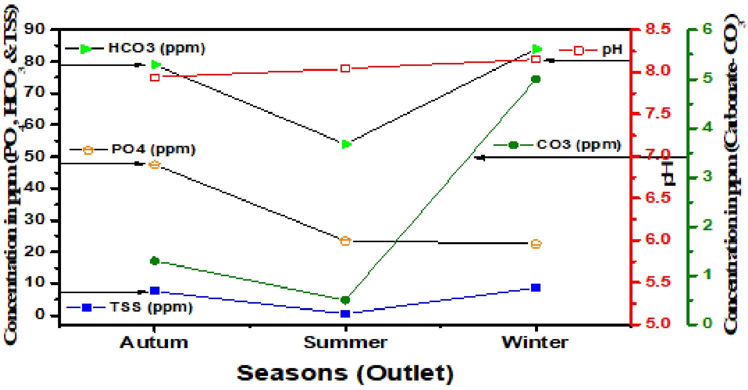

Fig.1c Seasonal effects on Physico-Chemicals parameters at outlet

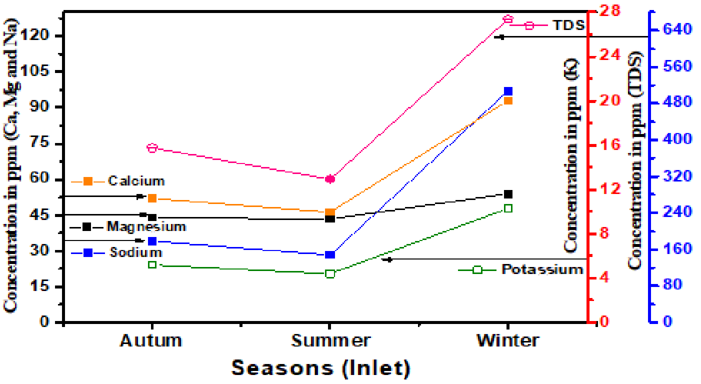

Fig.2a. Seasonal effects on TDS and cations at inlet

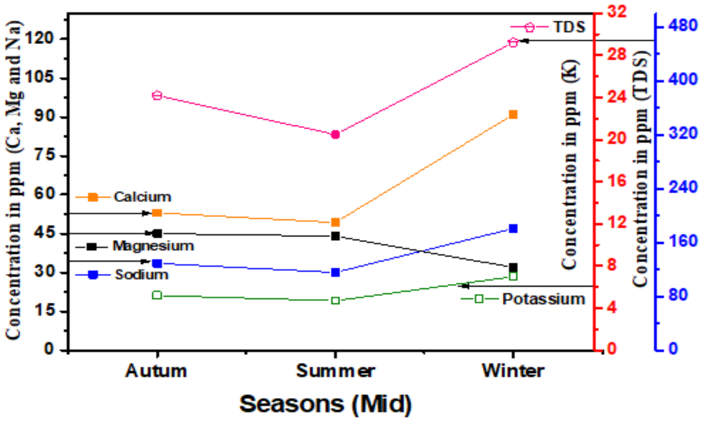

Fig.2b Seasonal effects on TDS and cations at Mid

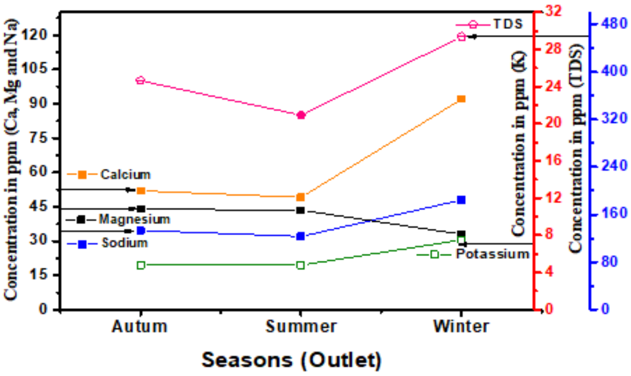

Fig.2c Seasonal effects on TDS and cations at outlet

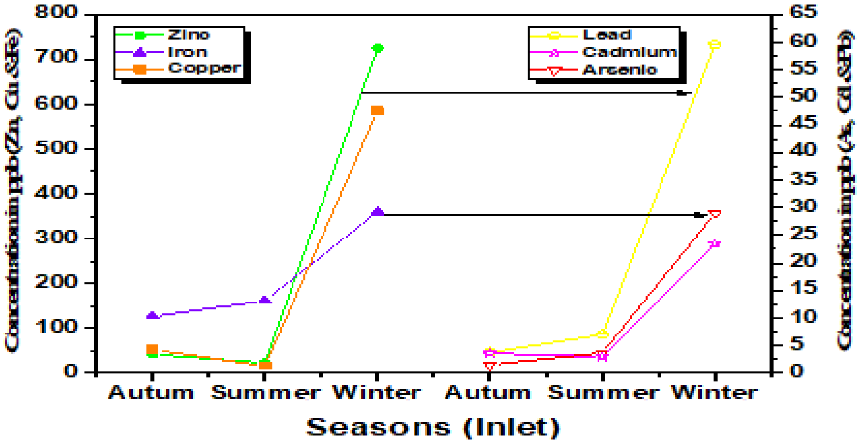

Fig.3a. Seasonal effects on Essential &Toxic Metals at Inlet

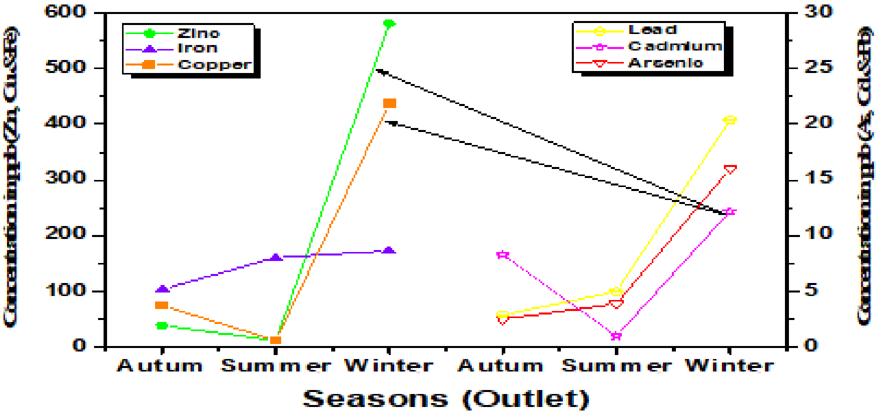

Fig.3b. Seasonal effects on Essential &Toxic Metals at Mid

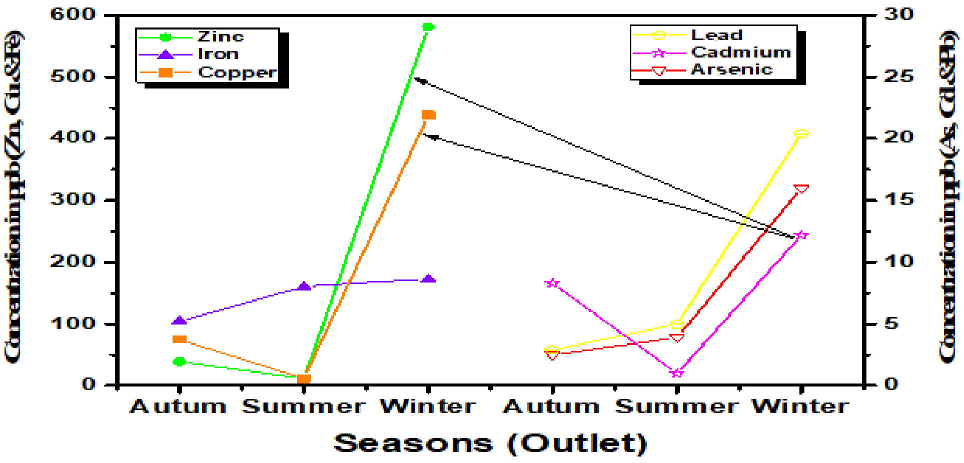

Fig.3c. Seasonal effects on Essential &Toxic Metals at Outlet

The rest of all samples were between ranges of 467 to 845µS/cm which were within the safe limits in table 1.TDS for all the sampling sites varied between314 mg/l to 665 mg/l, which was found within range of 1000 mg/L (That is permissible for occasional use only) as per table 1, but the recommended limit is 500 mg/L by WHO for continuous consumption. TSS results were found on higher side except sample no. 5 & 6. The results were measured between 0.5 mg/l to 9.6 mg/l. Cl results were found within guideline value of WHO as per table 1 between 38 mg/l to 157 mg/l. PO_4 results of all samples 21.4 to 45.3 mg/l were within permissible limits of (WHO 2011). SO_4 results were found between the ranges of 53 mg/l to 151 mg/l and were within safe limits. CO3 results were detected under permissible limit. The results were between 43 mg/l to 84 mg/l. Na was found in the range of 28.3 mg/l to 97 mg/l and found within the limits of EU directives as mentioned in table 1.Potassium (K)was detected between the ranges of 4.4 -10.3 mg/l and found within reasonable range. The Ca concentrations in our samples were found within legitimate range except samples 7, 8, 9 which were little higher such as 93, 91 and 92 mg/l which is due to flood effect. The results of Mg were also found within safe range 32 to 45 mg/l, excluding sample No. 7 which was 54 mg/l that indicate after flood effects as per table 1.Fe is the most commonly available metal on planet earth (Moscow *et al.*, 2011) andiron contents were found between the ranges of

0.101 to 0.376 mg/l, the sample No. 7 was found beyond the limit in 0.376 mg/l set as shown in table 2 (WHO, 2011).WhileCd was found in the range of 0.001 mg/l – 0.0235 mg/.Whereas the safe limit of Cd concentrations is0.003 mg/l. Here sample 3, 7, 8 and 9 exceeds the WHO guideline values mentioned in table 2. Sample 3 value which is a little higher than WHO limit may be due to previous year (2009) rains and sample 7,8 & 9 are much higher than WHO limits due to the historic flood from August to September 2010.Pb in trace amounts occur naturally in soil and water (Raviraja *et al.*, 2008). The permissible limit for lead in water is 0.01mg/L(WHO 2011). Even at low concentration it may cause developmental delay, miscarriages and low birth weight (Bellinger, 2005), in the current study lead was observed in the range of 0.005 to 0.0596 mg/l. All the higher values were found in three samples collected on 09-12-2010 after one and half month after flood.As is a great risks of lung and bladder cancer and skin changes. As was found in the limit of 0.001-0.029 mg/l, the safe limit (WHO 2011,), is 0.01 mg/l same as in case of Pb.Cr results were detected in the ranges of 0.009-0.149 mg/l. The permissible limit of chromium is 0.05 mg/l, which also followed the pattern of Pb and As.

Cu is an essential metal for all living organisms, plays an important role in many enzymatic reactions. The high concentration of Cu in water could cause epigastric burning, vomiting and diarrhea (Carson etal, 1987).The result of copper were found within the safe limits 0.012-0.586 mg/l, while the limit set by WHO is 02 mg/l.Zn was detected between the ranges of 0.13-0.583 mg/l and found within permissible limit (WHO 2011). The main source of Zn in water, use of fertilizers and pesticides of agricultural farms (Sarah *et al*, 2011).The seasonal and flood effects of pH, HCO_3, CO_3, PO_4 and TSS were compared in figure 1 a,b& c for inlet, mid & outlet respectively. Fig 1a, illustrate the dependence of CO_3 and HCO_3 on pH. CO_3 level at low pH is near zero and it increase with increase in pH above 7.5. HCO_3 behaves oppositely to CO_3, its concentration is highest at pH near to 7.5 and decrease with increase in pH. However, TSS grew in summer might be due to start of rains. The graph also depict that all the parameter dropped due to flood expect PO_4 which rose by a little after flood may be due to agriculture runoff mixing into flood streams. Figure 1b indicates change in HCO3 and TSS trend. Both the parameter increased with little rise in pH may due to change in incoming microorganisms diversification after flood. Similarly figure 1c trends are analogous tomid in figure 1b.Figure 2 a, b & c depict the cations and TDS trend at inlet, mid and outlet respectively. Figure 2a, shows seasonal and flood effect at inlet of the Lake. TDS declined from autumn to summer but shot up in winter due to flood effect. Ca, Mg and Na are the major contributors in TDS. The most effected cation is Na due to flood. Figure 2binfer the changes that could be observed in mid of the Lake are; that Ca markedly increases more than Na and Mg reduced after summer which may be due interaction of water constituents with the sediment including changes due to flood. Figure 2c, follows trend as presented in figure 2b. Hence it could be concluded that the Lake phenomena in predominant at mid and outlet but inlet water chemistry is more variable and vulnerable to environmental and climate changes. Figure 3 a, b & c illustrate the trends of essential (Zn, Fe & Cu) and toxic (Pd, Cd & As) metals in inlet, mid and outlet respectively. In figure 3a it can be clearly observed that Cu and Zn declined moderately in summer but Fe gradually rise from autumn to winter. On the other hand Pb and As are also dramatically increased but Cd slightly declined in summer only. All metals concentration rocketed after flood, which may be due to mixing of unmanaged industrial waste into flood stream. However, the trends of Zn is comparable with Pb and Fe with As Figure 3b the metal levels followed same pattern in figure 3a except change in trend of essential metal to toxic metals. Here at the mid Zn and Cu trends are comparable with Cd only may be due to dilution effect. Figure 3c shows similar picture as in figure 3b the only change is the higher concentration of Cd in autumn at outlet. Hence we can conclude from figure 3a, b & c that there is great threat related to heavy metals especially after flood and the trends between essential and toxic metals need be studied more deeply. We have compared essential metals with toxic metals including seasonal & flood effects.

Conclusion

The Lake water quality assessment helps to identify the significant parameters of getting better information about source of pollution. From the obtained results it is evident that, at present findings of the physico-chemical results of water quality of studied areas is found satisfactory and found within permissible limits (WHO 2011), except some chemical parameters and heavy metals like arsenic, cadmium, chromium and lead. It could be concluded that the water quality of studied area is affected potentially by human activities and flood. Nevertheless, it is recommended that dedicated precaution efforts should be taken for controlling the sources of water supplies to Keenjhar Lake in this area.After proper treatment of the water it can be used for drinking purpose and it is suitable for irrigation purpose without any treatment before flood. The analytical result of sample sites monitored in this study irrespective of pollution source the Lake water from these sampling sites required treatment to reduce the level of heavy metals concentration in drinking water before supply to the consumer. From the present study we are getting clear information that; the metal concentration are present in excess to WHO limits and is at the level which could be harmful. Hence the study suggest that the concentration of toxic metals are present in excess in all three locations after flood. It indicates precautionary measure, such as industrial waste management should be taken immediately to avoid the harmful effects.

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